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14. ABSTRACT
The objective of this research is advance the field of electric propulsion by producing and testing the first generation of fully scalable 2-D high-density electrospray emitter arrays microfabricated on porous metal substrates working in the purely ionic regime. Uniform porous 2D nickel arrays were fabricated with a pitch of 450 microns. These arrays were tested in the laboratory and display high IV characteristics. Ion fragmentation was identified as a source of inefficiencies, although moderate due to hot neutrals in the beam. MD simulations were carried out to describe the ion emission mechanisms. Device packaging was investigated using MEMS techniques.

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electrosprays, propulsion, porous metals, microfabrication

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Final Report
Grant FA9550-09-1-0274
(YIP-09) Fully Scalable Porous Metal Electrospray Propulsion

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February 2012

Research goal:

To advance the field of electric propulsion by producing and testing the first generation of fully scalable 2-D high-density electrospray emitter arrays microfabricated on porous metal substrates working in the purely ionic regime with variable specific impulse.

Summary of research objectives and findings:

The fundamental objective of this research sponsored by AFOSR was to improve the methods to fabricate micron-sized features on porous metals by investigating etch chemistries in metals compatible with ionic liquid propellants. Previous research indicated that the use of solid tungsten emitters is adequate as substrate material. However, porous tungsten is both expensive and in many instances unavailable with the required pore specifications. Instead, we focused on etching techniques that could be used in a variety of porous metals and, as baseline, selected nickel because it is available commercially at moderate costs.

In this research we identified a process to define photolithographically an array of dots on porous substrates that would be used as masks to etch emitter tips in two-dimensional arrays. Such configuration maximizes current density and therefore thrust density. Very importantly, we proposed and demonstrated that electrochemical etching could be used in porous metals provided etching rates are regulated by the diffusion of reaction products, otherwise etching could occur inside pores into the material bulk, thus preventing feature forming and promoting arbitrary substrate dissolution.

An important demonstration of this work was also related to the reason of changing the emitter fabrication from silicon to porous metals: in silicon, fluid transport is very inefficient given the poor wettability of ionic liquids on this material. Initial attempts tried to circumvent this difficulty by modifying the topology of the silicon substrate with nano-scale rough features (nano-grass, or black silicon). While appropriate for fluid distribution, such configuration forces liquid injection from the active (tips) side, which eliminates one of the most relevant features of this concept: potential compactness and no active propellant pumping system. Instead, it would be ideal to inject the propellant from the non-active substrate side (the back) and use capillarity alone through the bulk to supply the propellant to the tips on the active side. During the period of performance of this work, we demonstrated that such configuration and process is possible with porous metals, even if the raw wettability is not particularly good. In addition, capillary action is able to provide enough flow rate to all emission sites with no choking since the ability to extract current is limited by local dynamics at the Taylor cones formed on the emission tips on the active side.

Our team also demonstrated that 2D thruster architectures could be packaged in small silicon-based structures and 1 or 2 grids could be used. Additional work in this direction with particular emphasis on the variation of specific impulse for multi-modal propulsion is currently carried out by MIT and the Busek Company under an AFORS Phase II parallel study.

2D emitter arrays built on porous nickel have been tested with two ionic liquids: EMI-BF4 and EMI-Im. Their operational characteristics show very interesting phenomena previously not observed in other types of electrospray emitter sources. For instance, currents up to 5-10 μA per emitter tip were observed with no-saturating characteristics and steep IV curves of about 1 μA/V. This provides a useful control mechanism for a virtually constant Isp (weak variation with the square root of applied voltage) thruster at current levels that go from near zero (for potential missions requiring extreme precision in thrust delivery) to hundreds of $\mu A/cm^2$ (in current design) for missions that would require performance at higher powers, similar to what can be accomplished with state-of-the-art ion engines.

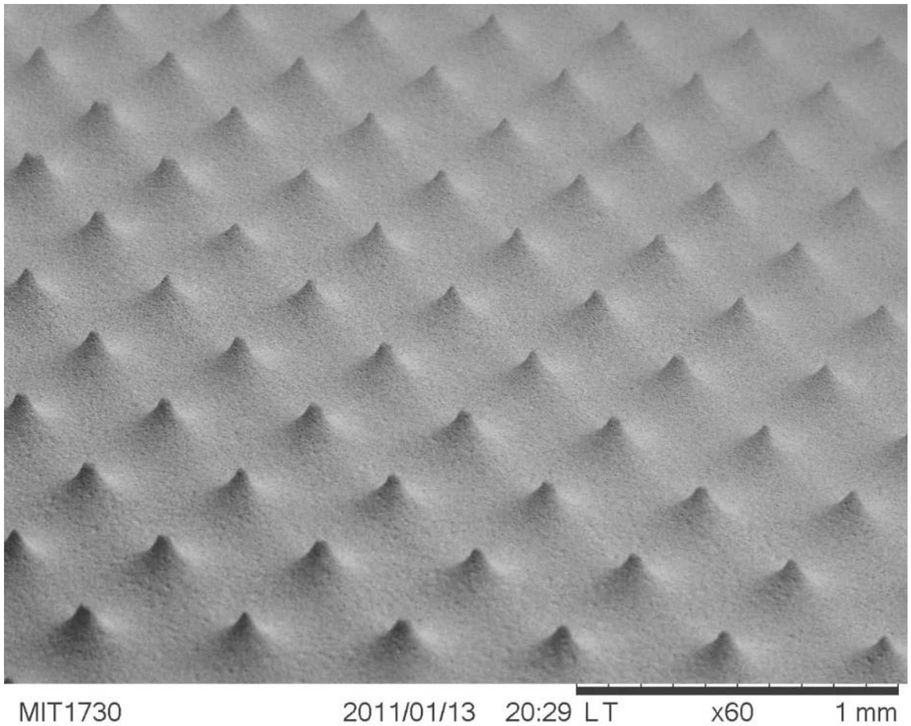
In addition, during the period of performance of this study our group started to look into molecular dynamics as a descriptive tool to understand better the process of field evaporation from ionic liquid surfaces. Initial work in this regard was based on published force fields, which have currently been challenged by new discoveries in this computational area. A parallel study has recently begun, also sponsored by AFOSR, to improve the accuracy and fidelity of MD simulation in the context of processes relevant for propulsion, such as the efficiency impact on the experimentally discovered metastability of solvated ions and the interaction of high energy species, including hot neutrals product of fragmentation events (solvated ion breakup), with materials of interest, such as MEMS-based materials that are used in the fabrication of miniature ion engines.

It is important to point out that during the period of performance of this YIP grant, a series of discoveries were made, such as a comprehensive determination of the energy structure of molecular ion beams and their reactivity due to the presence of active anions (like BF4, I, Cl, HF, etc.). These observations allowed our team to look into applications other than propulsion for this type of ion sources, such as reactive ion etching of semiconductor substrates and focused ion beam applications beyond gallium.

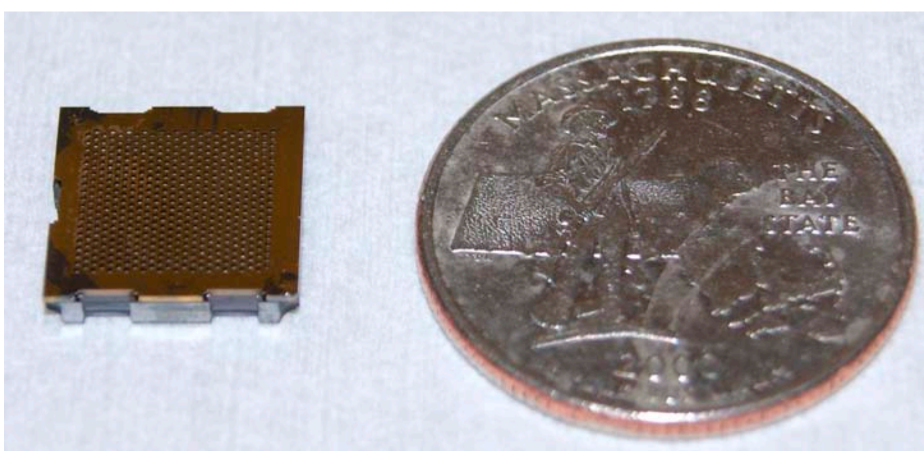
Finally, some preliminary thought was placed on possible applications of the techniques developed during this grant to propulsion for very small satellites, such as CubeSat nanosatellites. This was done mostly as an exercise on scalability as originally described in the proposal.

Graphic summary of the research:

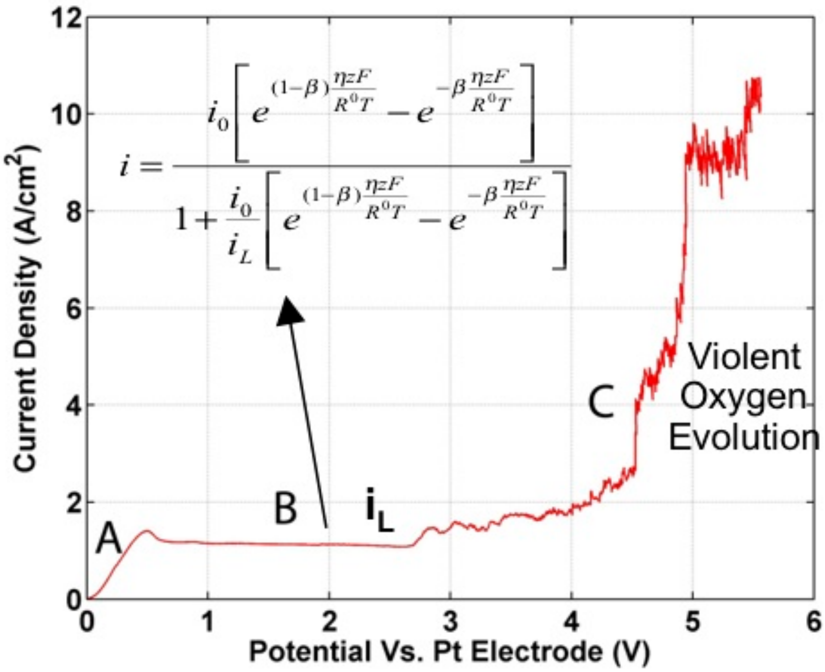
These pages illustrate graphically some examples of results accomplished during the period of performance of this research.



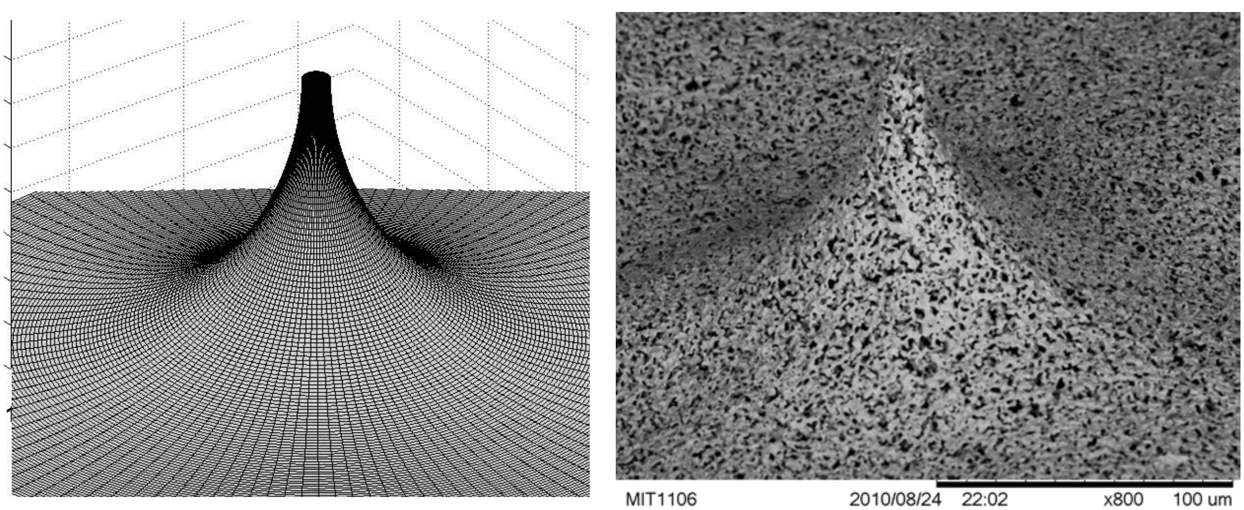
Example of microfabricated conical tips on porous nickel



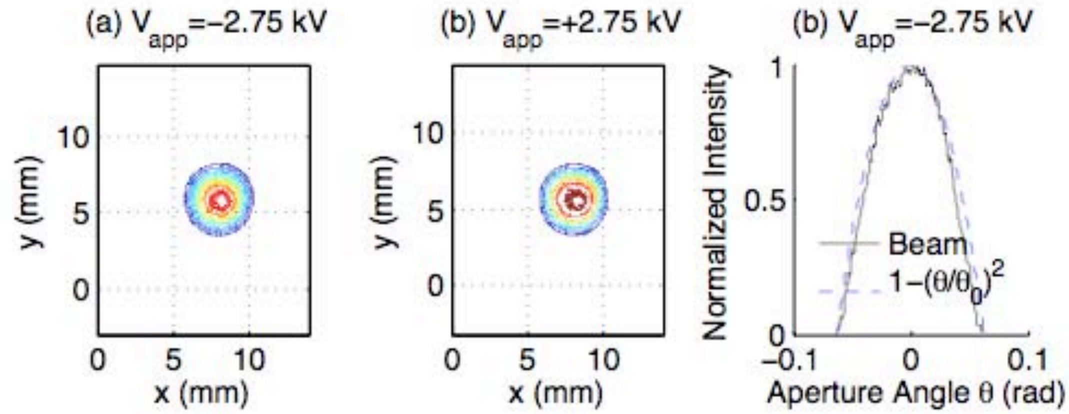
Fully packaged porous metal electrospray propulsion array



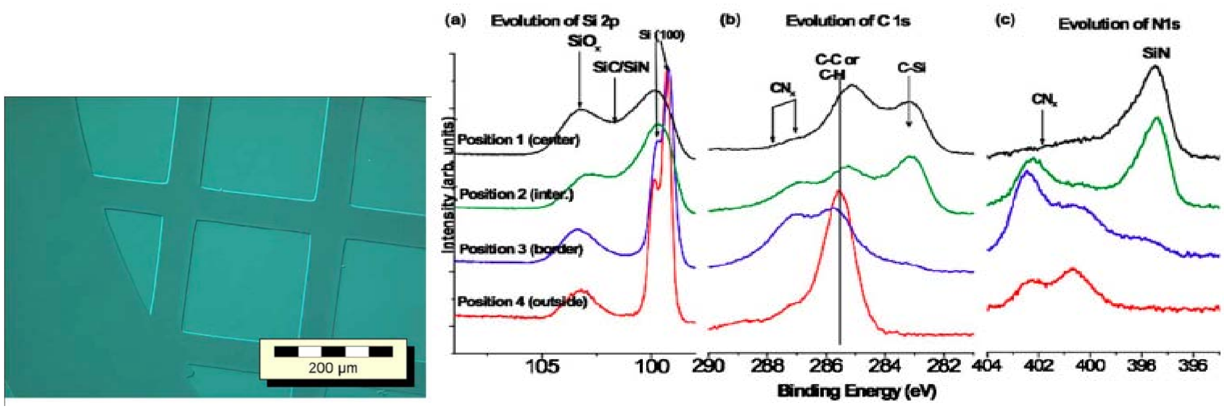
Current and extent of transport layers that enable microfabrication of micron-sized features on porous metals. Plot is for the couple nickel and hydrochloric acid.



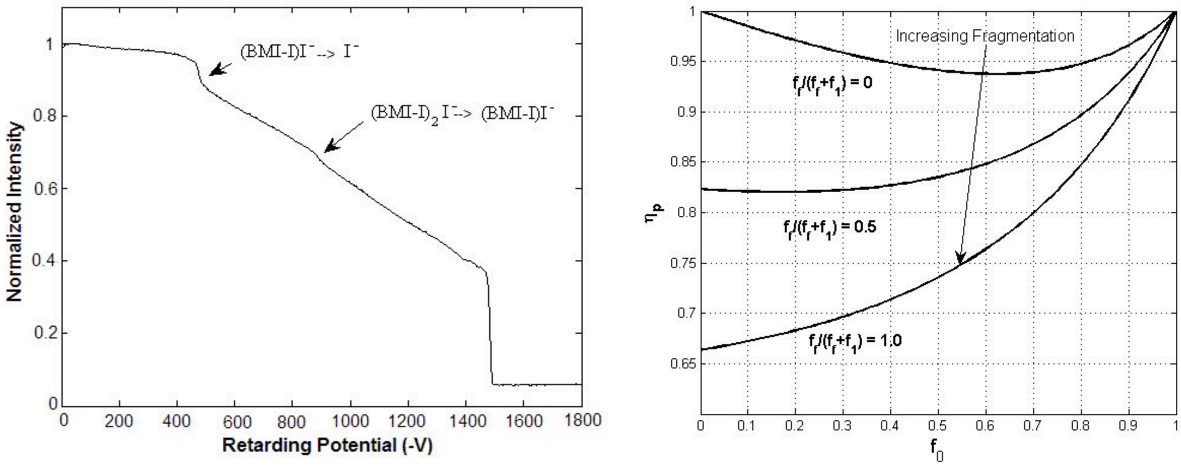
Numerical modeling of emitter shapes (left) correlated well with actual etched features (right). Models allowed us to identify best etching conditions and prevent wafer-level non-uniformities.



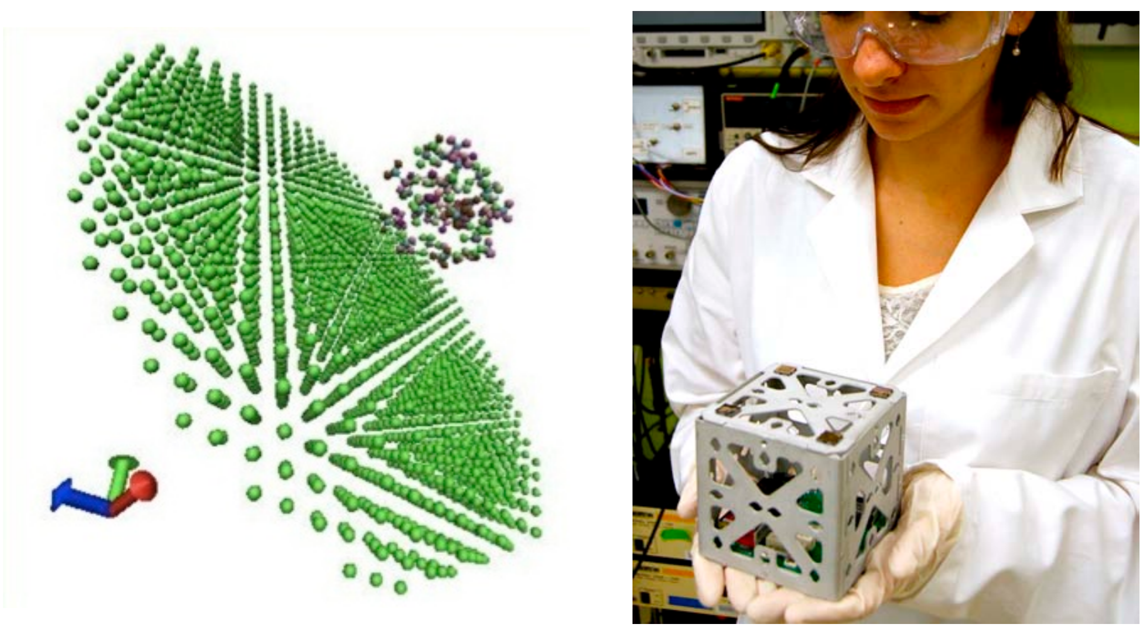
Beam profile distributions in the negative (left) and positive (center) modes as visualized directly thorough a multi-channel plate and phosphor screen. These profiles are parabolic (right) indicating the non-thermal character of these type of ion beams.



Microscopic Image of pattern imprinted on Si by an ionic liquid ion source (ILIS) at 15 keV (left) and XPS analysis of the area exposed to the ILIS beam (right). This indicates that F creates volatile species that enhance the etching rate, and that the Si reacts with the C and N atoms from the incident ions demonstrating reactive ion etching on semiconductors.



Signs of ion fragmentation distributed throughout the acceleration region. The measured energy signature (left) depends on the value of the local potential at the time of fragmentation for a beam of known initial energy. The effect on the performance of an electrospray thruster (right) is incorporated into the polydispersive efficiency via ion masses and fragmentation fractions. The conclusion is that hot neutrals avoid drastic reductions in overall efficiency.



Preliminary studies using molecular dynamics (left) have provided a way to probe the ion emission mechanisms. These and other tools developed in this research would eventually enable scalable electrospray propulsion applicable to a variety of different vehicles, including CubeSats (right) like the prototype shown here featuring 4 micro-thrusters and PPU.

Research outcomes:

The bulk of this research, including assumptions, analyses, processes, experiments and results are described in detail in 11 publications including the contributions of 10 people. This group includes students, researchers and faculty collaborators. These publications include 3 journal papers, 6 conference papers and 2 graduate level theses. Not included here are undergraduate thesis and a number of undergraduate-level projects, which were possible to sponsor with support from AFOSR. All these works are relevant in understanding the work structure of the 3-year period of performance. All of these works are available in the open literature, so the interested reader could look into the details of each research task. In the next paragraphs we will describe the contributions of each one of the 12 publications. The order is not necessarily chronological but rather describes the research sequence described above.

R. Legge and P. Lozano, Electrospray propulsion based on emitters microfabricated in porous metals, Journal of Propulsion and Power Vol. 27 No. 2 (2011) 485-495

Performance of microfabricated porous metal electrospray emitters is examined for a number of ionic liquid propellants and emitter clustering configurations. A method of creating dense arrays of miniaturized emitters using electrochemical etching microfabrication techniques is presented. Time-of-flight mass spectrometry and direct current measurements are used to characterize the emission of single emitters with four ionic liquids of different physical properties. Pure ion emission is observed for all ionic liquids tested. Results indicate that ionic liquids with lower ion masses produce more thrust at a given voltage than liquids with heavy ions due to a significant reduction in emitted ion current for the heaviest ions, likely caused by a combination of increased hydraulic resistance and slower charge relaxation times, respectively, due to higher viscosity and lower electric conductivity. Experiments with varying linear emitter array densities show that the current produced by individual emitters remains fairly constant, indicating that the thrust density can be increased with emitter miniaturization and clustering. A two-dimensional emitter array is constructed from three linear arrays and experiments show that the device produces an average current of around 1 μA per emitter at the highest voltages. Direct thrust measurements using a torsional balance show that the test fixture produces between 0.05 to 0.1 μN of thrust per emitter, as anticipated by theoretical estimates.

D.G. Courtney, H. Li, P. Diaz-Gomez, T.P. Fedkiw and P.C. Lozano, On the validation of porous nickel as substrate material for electrospray ion propulsion, AIAA-2010-7020, 46th AIAA/ASME/SAE/ASEE Joint Propulsion Conference, 25-28 July 2010, Nashville, TN.

The use of nickel as a substrate when creating porous metal Ionic Liquid Ion Source (ILIS) arrays for spacecraft propulsion has been explored and deemed viable. Nickel has been selected as a candidate material due to its compatibility with an electrochemical etching process specifically developed to yield surface micromachining of bulk porous metals without significant pore degradation. The investigation of nickel ILIS includes externally wetted emitters which were fabricated and compared with more common tungsten emitters. Using externally wetted emitters, beam currents measuring 100's of nA were detected for both positive and negative emission from two ionic liquids, EMI-BF4 and EMI-Im. The emission from EMI-Im was tested by time of flight spectrometry where it was confirmed that, under most conditions, the emission is purely ionic. In addition, the ionic liquid to nickel interface potential was probed during emission from externally wetted emitters. Here it was found that by alternating the emission polarity at frequencies on the order of 1 Hz, complete charging of the electrochemical double layer can be prevented. Combined with similar results from tungsten emitters it is motivated that detrimental electrochemical effects can therefore be suppressed through voltage alternation. The process implemented for electrochemically fabricating porous nickel ILIS arrays is presented along with a process for housing the array within a silicon enclosure which includes an aligned electrostatic grid. Finally, emission characteristics from a sample array of porous nickel ILIS are presented. Between 100 and 150 emitters fabricated on a 10 x 10 x 1 mm porous nickel wafer were fired yielding current levels up to 200 μA.

D. Courtney and P. Lozano, Characterization of Conical Ionic Liquid Ion Sources for 2-D Electrospray Thruster Arrays on Porous Substrates, Transactions of the Japan Society for Aeronautical and Space Sciences, Aerospace Technology Japan, Vol. 8 (2010) Pb73-78

Emission data from a new geometry of Ionic Liquid Ion Sources using porous materials are presented. Ionic liquids are molten salts at room temperature, which have near zero vapor pressure. Conical type emitters, fabricated on a planar porous substrate are well suited for high density 2-D arrays as they allow for both passive propellant feed through the bulk and simplified grid alignment compared with arrays formed from multiple emitter array substrates. This paper confirms that such conical emitters can provide beam currents of 100's of nA up to several μA with beams composed of pure ions with no charged droplets detected, as has previously been observed using alternative emitter geometries.

D. Courtney and P. Lozano, Porous ionic liquid ion source fabrication refinements and variable beam energy experiments, AIAA-2009-5087, 45th AIAA/ASME/SAE/ASEE Joint Propulsion Conference, 3-5 August 2009, Denver, CO.

This is paper presents new data demonstrating the ability to independently control emission current and beam energy using porous Ionic Liquid Ion Sources (ILIS) as electrospray thruster emitters. Following from previous research where flat strips of porous emitters were developed using tungsten substrates, this work employs similar emitters with both extraction and acceleration grids. Here two flat < 1 μm porosity tungsten arrays of 20 emitters each were configured within an ABS plastic body and aligned with tungsten grids. The emitter tip radii were between 20 and 30 μm. By controlling the grids independently, the net current emitted, along with the fraction of emitted current transmitted through the grids as a useful beam were monitored. The results indicated that while downstream acceleration of the beam had little impact on the emitted beam fraction, the ratio of current intercepted by the grids dominated decelerating energies less than 40% of the extracting potential. These experiments provide a baseline for developing constant power, variable specific impulse thrusters where high beam current fractions are desirable over a range of beam energies in order to maintain high thruster efficiencies. A modified fabrication process which employs dry photomasks is presented. The technique allows for high regularity between fabricated emitters and provides foundation for future developments of new emitter geometries. Currents per emitted ranged from 10s of nA up to roughly 0.4 μA at potentials of approximately 1.6 to 2.2 kV respectively.

D. Courtney and P. Lozano, Development of ionic liquid electrospray thrusters using porous emitter substrates, 27th International Symposium on Space Technology and Science, July 5-12, 2009, Tsukuba, Japan.

This is a paper describes some of the techniques used in etching 2D arrays of porous metals. Emphasis is placed on characterizing emissions at the single-emitter level, but the right geometry.

Fedkiw, T. and Lozano, P., Efficiency measurement of an ionic liquid electrospray thruster, Space Propulsion 2010, San Sebastian, Spain, 2010

Time of flight spectrometry and retarding potential analyzer measurements allowed our team to observe that solvated ion species (dimers, trimmers, etc) are metastable and are able to break uo in flight. It is found that such fragmentations occur both during ion acceleration and after full acceleration. There is an expected decrease in thruster efficiency in the case that ions break up before they fully accelerate due to the addition of polydispersivity to the beam as neutrals are created. Impact of neutral in propulsion are always detrimental, however, it is also found that in the acceleration region the rate of fragmentation is nearly uniform, and therefore neutral velocities are of the order of the parent ion. These hot neutrals contribute to trhust and therefore efficiency does not drop significantly, even in the case of full ion depletion. A parallel study sponsored by AFOSR will allow us to understand much better the nature of these fragmentation events, their characterization and impact on thruster efficiency.

Takahashi, N., Molecular Dynamics Modeling of Ionic Liquids in Electrospray Propulsion, SM Thesis, June 2010.

One challenge is to investigate in detail the mechanism for ion emission to complement experimental results and understand better how emission occurs in the micro to nano scale. Thus, atomistic modeling is used to understand properties of emitted charged particles which determine how the thrusters perform. As a preliminary study of ion emission from Taylor cones, ion evaporation from 3-5 nm droplets was observed in molecular dynamics (MD) simulations to validate the atomistic modeling and to investigate activation energies. Ion emission was examined in terms of internal and external electric fields and the activation energies of each case were obtained using Schottky's model and direct energy calculation to compare with experimental values. Ion emission was mainly observed with electric field strengths between 1.2 -2.0 V/nm and the emitted species include both solvated and non-solvated ions. Propulsive properties from Taylor cones are examined using results from the analysis of electric current from ion emission. In addition to an observation of ion emission from liquid droplets, numerical simulations for interactions between a solid plate and liquid droplets were conducted with MD simulation. It was concluded that another selection of force field needs to be considered to pursue further details, such as electrochemical effects.

Courtney, D., Ionic Liquid Ion Source Emitter Arrays Fabricated on Bulk Porous Substrates for Spacecraft Propulsion, June 2011.

If arrays of modest packing density (~5 emitters/mm2) could be achieved, ILIS as thrusters would offer a scalable form of propulsion capable of providing useful thrust levels to small satellites with performance comparable to established, but difficult to miniaturize, plasma based ion engines. This research has sought a technique for creating arrays of ILIS from bulk porous substrates as part of an overall process for microfabricating complete thrusters. The thesis includes a survey of potential fabrication methods considering both suitability for forming arrays of ILIS and the ability to integrate each technique within a thruster packaging process. Electrochemical etching is highly selective and can proceed at rates which are limited by mass transport conditions. In this thesis we show how this etching regime can be exploited to smoothly remove material from the surface of a bulk porous metal substrate without damaging the internal pore structure. Dry film photoresists have been identified as a suitable alternative to spin on techniques for porous materials and have been applied within an electrochemical etching process. A two step process for forming arrays of ILIS has been motivated using numerical simulations of the etching process to predict emitter profiles and investigate the impacts of non-uniform etching conditions. These concepts have been applied experimentally using a custom built, automated, etching station capable of repeatedly producing arrays of 480 emitters spaced 500 µm apart on a 1 x 1 cm porous nickel substrate pre-mounted, and aligned, within a silicon thruster package. The emitters are typically 165 _m tall with rounded tips suitable for operation as ILIS. Pulsed voltage conditions were found to significantly enhance wafer level uniformity enabling fabrication of functional emitters within a few hundred µm of the substrate boundary. The structures have been smoothed and rounded, making them suitable for use as ILIS, during a secondary etch process using electrolytes doped with nickel chloride to suppress transient effects. These doped solutions enabled a few µm of material to be removed selectively from the porous surface while maintaining smooth features. These arrays have been mounted and aligned with electrostatic grids to demonstrate their emission capabilities. Propellant has been fed to the emitters by capillarity within the porous bulk and then extracted at potentials as low as 850 V. Beam currents exceeding several 100 µA at both positive and negative polarities have been measured using both EMI-Im and EMI-BF4 ionic liquid propellant. Two complete devices were tested yielding large beam currents and very high transmission fractions (88-100 %) from both attempts. We estimate that these devices can supply 10's of µN of thrust at modest operating potentials, ~1.5 kV, with a specific impulse of roughly 2000-3000 s. When completely packaged, the thrusters measure 1.2 x 1.2 x 0.2 cm, weigh less than 1 g and require less than 0.65 W of operating power.

N. Takahashi and P. Lozano, Atomistic simulations of electrospray ion emission from a tungsten plate, AIAA-2009-5089, 45th AIAA/ASME/SAE/ASEE Joint Propulsion Conference, 3-5 August 2009, Denver, CO.

A preliminary numerical study for electrospray thrusters is carried out including the interaction between solid tungsten and the ionic liquid, 1-ethyl-3-methyl imidazolium tetrafluoroborate (EMI-BF4). Classical molecular dynamics is used to investigate the behavior of a nano-droplet of EMI-BF4 on a tungsten plate. The diameter of the droplets are approximately 1 and 2 nm, which includes 8 and 27 EMI-BF4 molecules, for a total of 192 and 648 atoms. As for the tungsten plate, the thickness and the diameter are approximately 1 nm and 7 nm, respectively. Following the equilibration of the tungsten-ionic liquid system, a strong electric field is applied in two ways: by assuming a constant and uniformly distributed electric field and by assigning charges to the tungsten atoms, thus simulating a surface charge distribution. Ion emission is observed from the liquid in both cases.

C. Perez-Martinez, S. Guilet, J. Gierak and P.C. Lozano, Ionic liquid ion sources as a unique and versatile option in FIB applications, Microelectronic Engineering 88 (2011) 2088-2091

This work discusses the potential applicability of point sources to focused ion beam (FIB) technology based on molten salts at room temperature, known as ionic liquid ion sources (ILIS). The beam shape and divergence angles for ILIS using the ionic liquid EMI-BF4 (1-ethyl-3-methylimidazolium tetrafluoroborate) are reported, as well as the stability of the source in an alternating polarity regime. It is found that beam profiles are parabolic and are non-thermal in nature, as previously anticipated. This is relevant to satellite operators as the beam density practically goes to zero outside the envelope. Stable emission from ILIS using the liquid BMI-Im (1-butyl 3-methylimidazolium imide) was obtained, and the energy characteristics of the full beam are presented. A magnetic filter is proposed to separate the ion beam by degrees of solvation to determine the energy characteristics of individual species.

D. Courtney and P. Lozano, Porous ionic liquid ion source thrusters for small satellite Propulsion, Canadian Aeronautics and Space Institute 15th Astronautics Conference, ASTRO 2010, May 4-6 2010, Toronto, Ontario, Canada

This is one of our papers describing systems-level scalability of electrospray propulsion in the pure ionic regime to nanosatellites. A series of maneuvers are described together with power considerations.

P.C. Lozano and D. Courtney, On the development of high specific impulse electric propulsion thrusters for small satellites, 1915685, The Small Satellites Systems and Services – The 4S Symposium, Funchal, Madeira, Portugal, May 30 – June 4, 2010

The fundamental working principles and preliminary engineering design of electrospray-based electric propulsion systems for small satellites are presented. The applicability of this technology is discussed in the context of a series of examples of expected performance on CubeSat vehicles.

Conclusion

This 3-year project was essential in the development of a scientific understanding of scalable electrospray propulsion based in porous metals. In turn, this scientific understanding would eventually enable the application of this technology to a variety of missions. There were no serious bottlenecks precluding our team from obtaining essential information in this project, both experimentally and theoretically. The results summarized in this report are described in detail in hundreds of pages published in the open literature. One of the most important contributions has been the identification of new research directions required for future development of electrospray propulsion science and technology.

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